

# Exhaust Emissions and Health Effects of Particulate Matter from Agricultural Tractors Operating on Rapeseed Oil Methyl Ester

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**ABSTRACT:** Exhaust emissions and their effects on the environment and human health, such as mutagenicity of particulate matter (PM) and ozone-forming potential, must be considered when using an alternative fuel. In the present work, a test engine and two agricultural tractors ran on rapeseed oil methyl ester (biodiesel) or conventional diesel fuel as well as blends thereof. The objective was to detect any disproportionately positive or negative effects depending on blend levels, because conventional diesel fuel and biodiesel can be blended in every ratio. Generally, emissions of regulated compounds changed linearly with the blend level. The known positive and negative effects of biodiesel varied accordingly. Overall, no optimal blend was found. Increasing biodiesel content of the fuel caused a linear increase in benzene emissions in the agricultural five-mode engine test, an effect that may be explained from previous studies on precombustion chemistry. In using the test engine, it was found that PM from biodiesel significantly reduced mutagenic potential compared with that from diesel fuel, although in this work PM masses were found to be reproducibly higher for biodiesel from rapeseed oil compared with conventional diesel fuel. Ozone precursors increased 10–30% when using biodiesel compared with conventional diesel fuel. Emissions of aldehydes and alkenes are mainly responsible for this effect. N<sub>2</sub>O emissions increased when using a catalytic converter.

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**KEY WORDS:** Biodiesel, exhaust emissions, nitrogen oxides, particulate matter, rapeseed methyl ester.

Biodiesel, defined as the monoalkyl esters of vegetable oils or animal fats, is being used as an alternative fuel in many conventional diesel engines (1,2). In Germany and other European countries, biodiesel usually is rapeseed oil methyl ester (RME), which is derived from low-erucic acid rapeseed oil and is often termed canola oil, whereas in the United States it is mainly soy methyl ester. However, even the combustion of “green” fuels such as biodiesel leads to emissions of hazardous gaseous compounds and particulate matter that may affect human health.

Diesel engine exhaust (DEE) has been classified as carcinogenic to experimental animals and as a probable carcinogenic

agent to humans by the International Agency for Research on Cancer (3). Several studies reported an increased relative risk of approximately 50% for lung cancer by DEE after long-term exposure (4). The carcinogenic effect of diesel exhaust is attributed mainly to the inhalation of soot particles (5). Many known or suspected mutagens and carcinogens, as, for example, polycyclic aromatic hydrocarbons (PAH), are adsorbed onto the surfaces of carbon cores of DEE particulate matter (PM) as organic phase (6,7). Because of their median dynamic diameter (0.1–0.3  $\mu\text{m}$ ) the particles are readily inhaled, and about 10% are deposited in the alveolar region of the lungs (5).

In the United States, soybean oil-derived biodiesel successfully completed Tier I and Tier II Health Effects testing (8). Evaluation of the results shows that biodiesel offers significant health benefits compared with conventional diesel fuel (DF) because most exhaust emissions are significantly reduced. The present work compares PM emissions from conventional DF with those from rapeseed oil-derived biodiesel regarding emitted masses as well as particle size and particle number distributions. To estimate the physiological effects of PM from DF and RME, mutagenic potentials were determined. The potential influence of biodiesel exhaust emissions on ozone formation in the troposphere relative to those from DF was also studied. Because biodiesel and conventional DF are miscible in every ratio, different blend levels ranging from neat biodiesel to neat conventional DF were evaluated. Different blend levels are used and recognized as alternative diesel fuels in numerous countries around the world with the use of specific blend levels depending on economic and regulatory environments.

## EXPERIMENTAL PROCEDURES

*Engines and test cycles.* The test engine chosen was Farymann (Mannheim, Germany) engine type 18 D, an air-cooled 4.2 kW one-cylinder four-stroke diesel engine with direct injection. All tests were carried out with and without an oxidation catalytic converter. Technical data are given in Table 1. Three replicates were run of each test and the averages are reported here. Because of its convenience, the Farymann engine (normally used in construction equipment and emergency power generators) was used for the extended series of investigations with different blends. Additionally, a Fendt

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**TABLE 1**  
**Technical Data of the Test Engine Farymann Type 18 D**  
**and the Fendt Tractor MWM Type D 226.4.2**

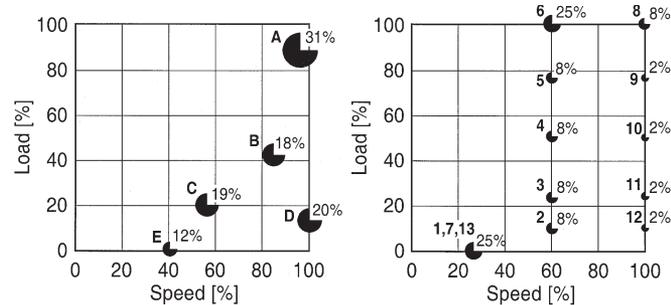
Engine	Farymann 18 D	Fendt tractor
Stroke of cylinder	55 mm	120 mm
Bore of cylinder	82 mm	105 mm
Number of cylinders	1	4
Stroke volume	290 cm <sup>3</sup>	4154 cm <sup>3</sup>
Normal rate of revolutions	3000 rpm	2200 rpm
Rated power	4.2 kW	52 kW
Maximum torque	15.2 Nm at 2200 rev/min	266 Nm at 1500 rev/min
Compression ratio	1:20	1:16

tractor type 306 LSA with direct injection diesel engine (type MWM D 226.4.2) was used for testing. It was equipped with a special catalytic converter (Oberland Mangold, Garmisch-Partenkirchen, Germany) for biodiesel. Technical data for the tractor are also given in Table 1. The tractor was used for the investigation of ozone precursors and particulate matter emissions. The German agricultural five-mode cycle was chosen as engine test-cycle. This cycle has no legislative foundation, but simulates the typical load of agricultural tractors in Germany (9) (see Fig. 1; relative times shown).

**Fuels.** RME complying with the German standard DIN E 51606 was provided by Connemann Company (Leer, Germany) and with 370 ppm sulfur DF by German Shell (Hamburg, Germany). The FA composition (vol%) of the RME used for experiments with the Fendt tractor was as follows: 16:0 = 4.60, 16:1 = 0.19, 18:0 = 1.68, 18:1 = 59.94, 18:2 = 21.06, 18:3 = 8.93, 20:0 = 0.55, 20:1 = 1.44, 20:2 = 0.07, 22:0 = 0.35, 22:1 = 0.60.

**Analytical equipment.** All regulated gaseous compounds were taken directly out of the undiluted exhaust gas stream and were measured with customary analyzers as discussed in the literature (10,11). PM was sampled from a double isokinetic dilution tunnel (12). It was collected on polytetrafluoroethylene-coated glass fiber filters (T60A20; Pall Co., Dreieich, Germany). Volatile organic matter was determined by heating the filters for 24 h at 220°C. Tests revealed that this method gives results comparable to Soxhlet extraction with dichloromethane (12).

Methane and nitrous oxide were measured by high-resolution FTIR spectroscopy on a Magna 550 instrument (Nicolet,



**FIG. 1.** Modes of the agricultural five-mode test in comparison with the heavy-duty 13-mode cycle (ECE R-49).

Offenbach, Germany) with a long-path gas cell. Spectra were analyzed by fitting sets of calibration spectra. Besides methane and nitrous oxide, nitrogen oxide and nitrogen dioxide were also determined. The results of nitrogen oxides (NO<sub>x</sub>) determination agreed with those of the chemiluminescence detector. Benzene was determined by GC on a Varian Star 3600 CX instrument (Varian, Palo Alto, CA) equipped with an FID.

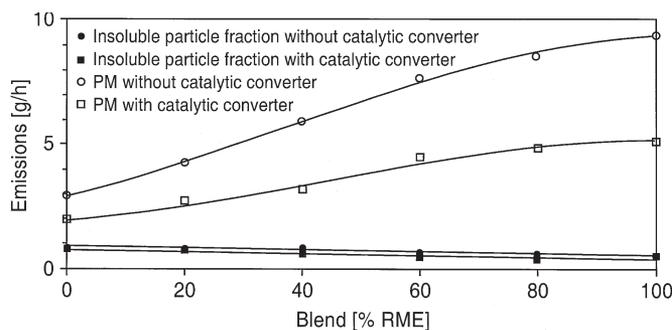
For particulate matter analyses, a Scanning Mobility Particle Sizer (SMPS) model 3934 with a Condensation Particle Counter (CPC) Model 3010 obtained from TSI Company (Aachen, Germany) (13) was used. The SMPS system separates particles in the range of 7–300 nm. In this range, particles were divided into more than 100 different sizes by electrostatic mobility.

Ozone precursors and aldehydes were determined by HPLC on a Hewlett-Packard (Überlingen, Germany) apparatus. Analyses of alkenes and alkynes were performed by GC on a Shimadzu (Duisburg, Germany) 17A gas chromatograph equipped with a Chrompack (Vlaardingen, The Netherlands) CP 4020 cryotrap.

## RESULTS AND DISCUSSION

**PM relative to blends.** With and without catalytic converter, in most cases PM increased linearly with increasing RME percentage. The greatest increase was found between 40 and 60% RME (Fig. 2). Nonlinearity appeared only in mode C, whereas all other modes showed linear dependency (14). As expected owing to the well-known reduction of soot by RME (9), insoluble organic matter decreases with higher percentage of RME. This effect correlated linearly with the blend level. Statistical analysis gave  $R^2 = 0.81$  with catalyst and  $R^2 = 0.80$  without catalyst. It may be noted that many exhaust emissions studies reported decreases in PM from biodiesel compared with conventional DF (for an overview, see Ref. 1). It is possible that this discrepancy can be attributed to differences in the composition of the fuels being compared, likely the conventional DF used as comparison.

**Nitrous oxide relative to blends.** NO<sub>x</sub> exhaust emissions did not differ with fuel (Fig. 3). This result coincides with other



**FIG. 2.** Emissions of particulate matter and insoluble organic matter with and without catalytic converter for different blends; Farymann test engine, five-mode test. PM, particulate matter; RME, rapeseed oil methyl ester.

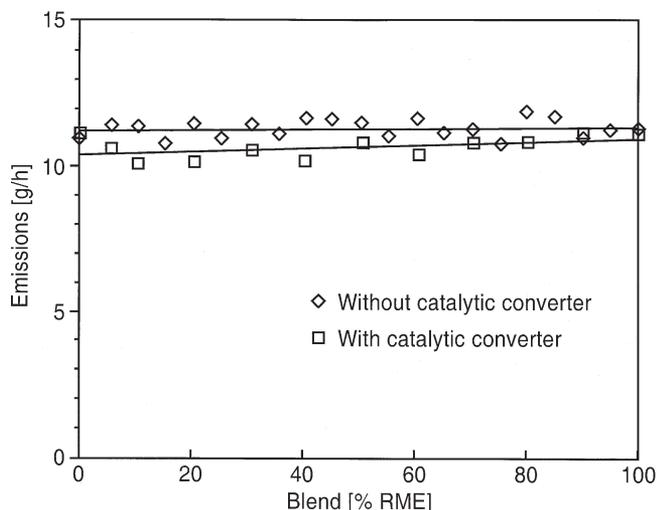


FIG. 3. Emissions of  $\text{NO}_x$  with and without catalytic converter (five-mode test cycle). See Figure 2 for abbreviation.

work that showed that  $\text{NO}_x$  exhaust emissions are either approximately equal to or slightly increased when using biodiesel instead of conventional DF. However, other studies usually did not take the effect of a catalytic converter on  $\text{N}_2\text{O}$  species into account. In the present work, it was found that the catalytic converter affected emissions, especially  $\text{N}_2\text{O}$ . In sum of the test cycle, the  $\text{N}_2\text{O}$  emissions doubled (Fig. 4) with the increase mainly due to mode B. Intake air temperature may also influence the results. Comparative test series in winter (low temperatures and low humidity) and in summer (high temperatures and high humidity) revealed considerable effects on  $\text{N}_2\text{O}$  emissions.

As mentioned above, numerous other studies on exhaust emissions from biodiesel use showed that  $\text{NO}_x$  exhaust emissions are either slightly increased or comparable to those from conventional DF (for reviews, see Refs. 1 and 2). This is the case despite the higher cetane number of biodiesel compared with conventional DF. In particular, studies on the effects of cetane-improving additives showed that  $\text{NO}_x$  exhaust emissions usually are reduced when the cetane number of a diesel fuel increases (15). This observation implies that an addi-

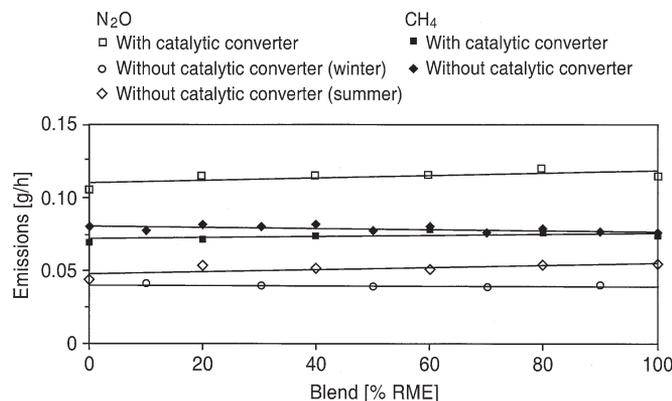


FIG. 4. Emissions of nitrous oxide and methane with and without catalytic converter for different blends; Farymann test engine, five-mode test. See Figure 2 for abbreviation.

tional mechanism or mechanisms may have an effect on  $\text{NO}_x$  formation besides the mainly prevalent thermal Zeldovich mechanism (16) when using biodiesel.

**Methane relative to blends.** Neither the blend level nor the presence of a catalytic converter influences methane emissions. The low conversion rate for neat DF decreased linearly to zero for neat RME (Fig. 4). Methane and other short-chain hydrocarbons (HC) were detected in other investigations of transient exhaust emissions (17,18).

**Benzene relative to blends.** Benzene emissions increased with the amount of RME, although, in contrast to DF, RME does not contain benzene. This finding indicated that the benzene content of fuels is not necessarily the main source of benzene in exhaust emissions. The catalytic converter reduced the emission by one-third (Fig. 5). Statistical analysis yielded  $R^2 = 0.80$  without catalyst and  $R^2 = 0.95$  with catalyst. In this connection, precombustion chemistry studies of neat fatty esters injected into a constant-volume combustion apparatus simulating the conditions in a diesel engine showed that aromatic compounds (benzene and alkylbenzenes) vary somewhat in dependence on the amount of unsaturation in the fatty compound (19). More highly unsaturated compounds form slightly greater amounts of aromatics. The higher content of unsaturated compounds in RME compared with conventional DF could explain the slightly higher benzene emissions when using fuels with increasing amounts of RME.

**Particle size and particle number distributions.** Up to the present time, PM mass has been the regulated value. Recently, particle number and particle size distributions were recognized as being more important than mass because one particle of 1- $\mu\text{m}$  diameter has the same mass as 1000 particles of 0.1  $\mu\text{m}$ . Small particles reach pulmonary alveoli and are deposited there, whereas larger particles are deposited in the upper airways and eliminated by the ciliated epithelium of the airways (3). Ultrafine particles (<100 nm) are considered to be especially critical to human health (20). Therefore, a SMPS/CPC-system was used to measure the number of different particle-size fractions. The experiments were carried out on the Fendt tractor.

The particle size distribution of RME, DF, and RME with catalytic converter is presented as weighted result of the five-mode cycle in Figure 6. The maximum of the particle distribu-

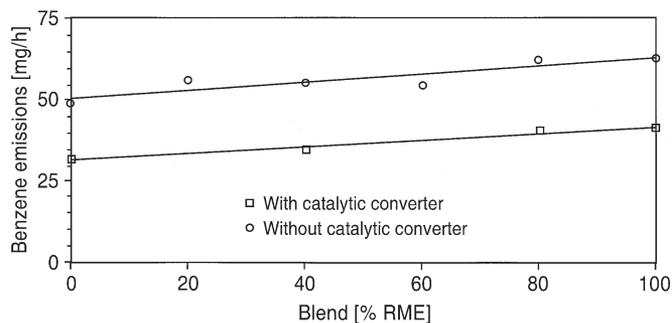
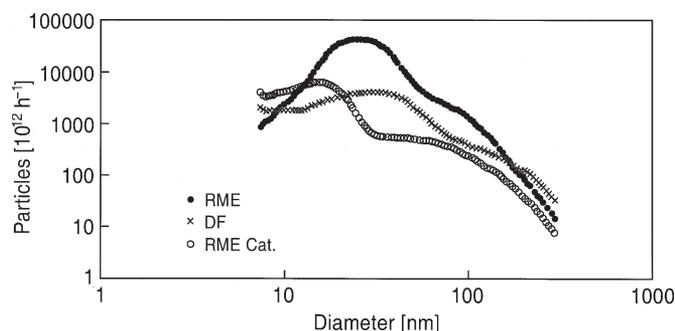


FIG. 5. Emissions of benzene with and without catalytic converter for different blends; Farymann test engine, five-mode test. See Figure 2 for abbreviation.



**FIG. 6.** Particle number distribution of RME, diesel fuel (DF), and RME with catalytic converter (RME Cat.); Fendt tractor, five-mode test. See Figure 2 for other abbreviation.

tion is at 30 nm for DF. A shift to slightly smaller particle sizes is observed for RME (maximum at 27 nm). Moreover, the particle number for RME is higher over the whole range. The catalytic converter reduces the particle number and the maximum of the particle distribution (maximum at 16 nm).

Because of some irreconcilable results of particle-size distributions in individual modes relative to the weighted result of the five-mode test, each mode is depicted separately in Figure 7. In modes A and E, the shapes of the particle number distributions were comparable. Absolute particle numbers of RME and DF were similar in mode A. However, RME caused more particles in mode E. The catalytic converter reduced particle numbers in both modes. The maximum was at 100 nm (mode A, DF and RME), 65 nm (mode A, RME with catalytic converter), and 40 nm (mode E). In modes B, C, and D, the shapes of the distribution curves differ depending on the fuel or the exhaust treatment. In modes B and D, RME increased emissions of small particles, but the catalytic converter reduced these smaller particles more effectively than it did the larger ones. However, the catalytic converter caused a shift toward smaller particles. This indicates that the smaller

particles may be liquid, probably unburned fuel, easily eliminated by the catalytic converter. In contrast, the larger particles may have a solid core that cannot be oxidized. These theoretical considerations correlate with results obtained with an impactor (not shown here), in which case the smaller particles were eliminated well by the catalytic converter (21).

**Mutagenic effects of PM.** For pollutant evaluation, biological effects are of fundamental importance. Therefore, the mutagenic activity of diesel engine exhausts from RME and DF was studied. Organic extracts of filter-collected particulate from DEE act as mutagens in bacterial and mammalian *in vitro* assays. Most investigations were performed using the *Salmonella typhimurium*/mammalian microsome assay (6,22,23). This test detects mutagenic properties of a wide spectrum of chemicals by reverse mutations of a series of *S. typhimurium* tester strains, bearing mutations in the histidine operon. This results in a histidine requirement of the tester strains in contrast to wild-type *S. typhimurium*. The Ames test (22) is the most frequently used test worldwide for investigating mutagenicity of complex mixtures such as combustion products. The present study employed the revised standard test protocol (24) with the test strains TA98 and TA100. According to the criteria given by Ames *et al.* (22), results were considered positive if the number of revertants on the plates containing the test concentrations was twice the spontaneous reversion rate and a reproducible dose-response relationship was observed. The present analytical procedure was described more extensively by Krahl *et al.* (25).

Collected PM masses differed widely depending on engine loads and fuels. In most tests, collected masses from RME exhaust were higher than those from DF. Higher percentages of sampled masses were extractable from the filters for RME than from those used for petroleum DF (Table 2). This observation is likely due to a smaller content of soot in biodiesel exhaust emissions, as shown previously (9,10) for investigations carried out on the Farymann test engine.

**TABLE 2**  
Sample Weights of Particulate Matter and Results of Soxhlet Extractions; Farymann Test Engine, Five-Mode Test<sup>a</sup>

Modes of the five-mode test		A (rated power)		B (partial load)		C (partial load)		D (partial load)		E (idle motion)	
		DF	RME	DF	RME	DF	RME	DF	RME	DF	RME
Sample weight (mg)	Filter										
	1	11.5	11.3	4.2	17.3	7.5	35.4	9.0	36.2	6.1	13.3
	2	10.8	11.1	5.0	16.6	8.3	35.7	10.0	34.3	7.7	16.6
	3	10.8	11.3	5.2	16.3	9.8	30.6	10.5	32.9	8.2	14.0
	Mean	11.0	11.2	4.8	16.7	8.5	33.9	9.8	34.5	7.3	14.6
Extractable matter (mg)	Filter										
	1	3.9	8.2	3.4	16.4	7.1	35.2	8.6	36.0	5.6	13.3
	2	3.3	8.2	3.7	16.3	7.5	35.7	9.5	33.9	7.0	16.4
	3	3.0	8.0	3.9	15.8	9.0	30.5	10.2	32.6	7.9	14.0
	Mean	3.4	8.1	3.7	16.2	7.9	33.8	9.4	34.2	6.8	14.6
Extractable matter (%)	Filter										
	1	34	73	80	95	95	99	96	99	92	100
	2	31	74	74	98	90	100	95	99	91	99
	3	28	71	75	97	92	100	97	99	96	100
	Mean	31	73	76	97	92	100	96	99	93	99

<sup>a</sup>DF, diesel fuel; RME, rapeseed oil methyl ester.

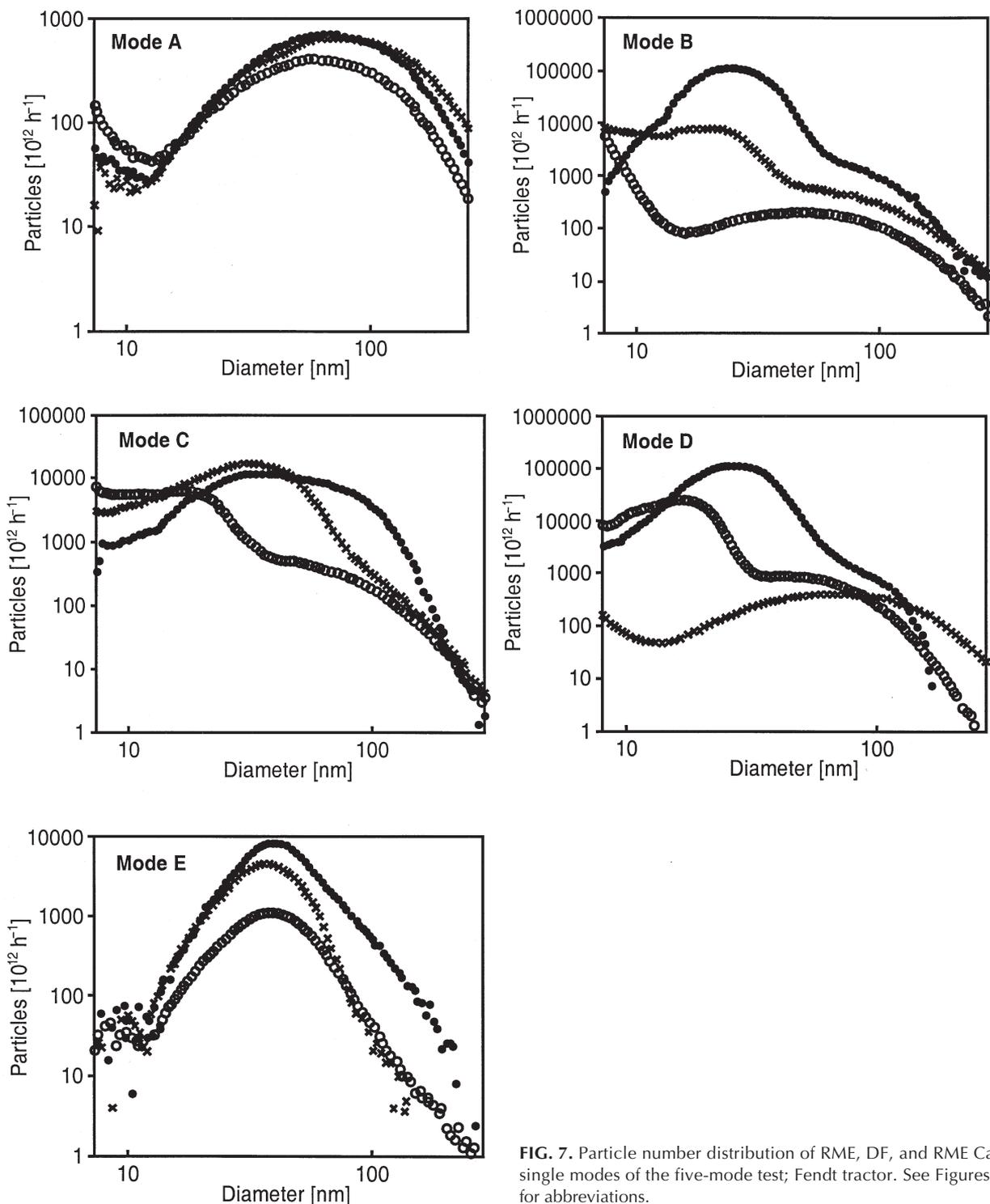
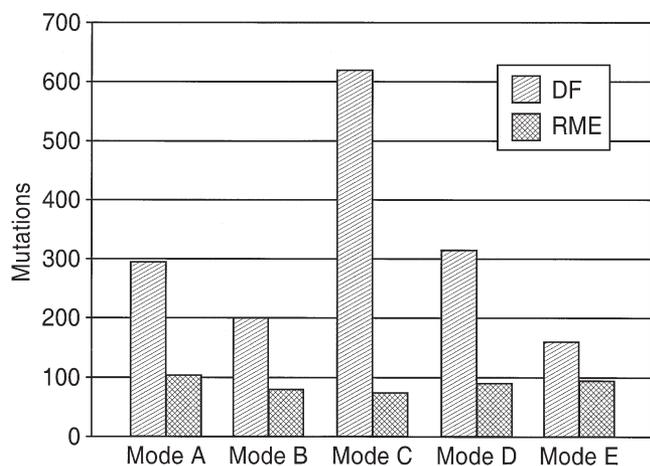


FIG. 7. Particle number distribution of RME, DF, and RME Cat. in the single modes of the five-mode test; Fendt tractor. See Figures 2 and 6 for abbreviations.

A significant increase of spontaneous mutations was obtained in the test strain TA98 for both fuels. However, for DF the revertant frequencies were two- to eightfold higher compared with those for RME (Fig. 8). Revertant frequency was also significantly elevated in the test strain TA100, and the mutations using DF were two- to threefold higher than those for RME. Testing with activated liver enzyme S9-fraction slightly decreased the number of revertants in most experi-

ments. These results indicated a higher mutagenic potential of DEE from DF compared to RME. This is probably due to the lower content of PAH and soot in the exhaust, although the emitted masses from RME were higher at most loads.

It may be noted that, despite discrepancies in the PM mass reported here compared with other studies (higher vs. lower PM mass compared with conventional DF), biodiesel (from either rapeseed oil or soybean oil) has beneficial health effects

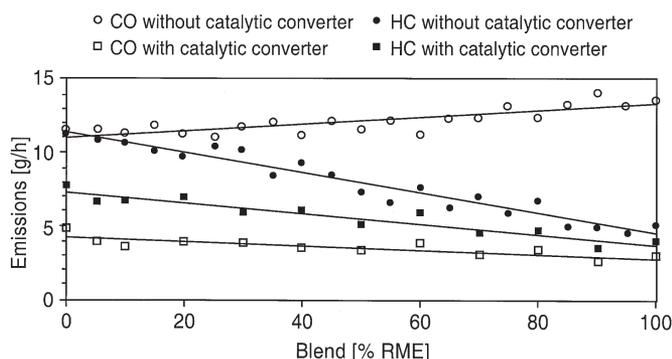


**FIG. 8.** Number of mutations from extracts of RME exhaust particles on test strain TA98 compared with DF in the five-mode test (number of spontaneous mutations = 32 per plate); Farymann test engine, five-mode test. See Figures 2 and 6 for abbreviations.

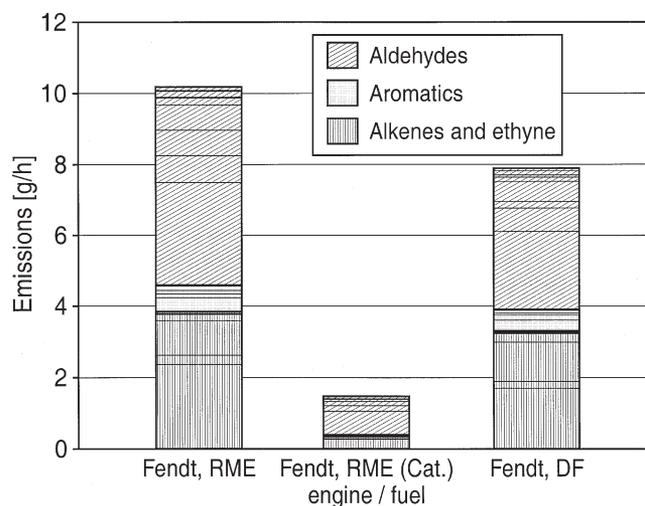
as shown by the present results and the Tier 2 Health Effects tests (8).

**Regulated gaseous compounds and ozone precursors.** In summer, ozone is one of the main air pollutants. Traffic contributes to ozone formation especially in urban areas, because the photochemical reaction of components of exhaust emissions, such as volatile organic compounds, yields ozone in presence of  $\text{NO}_x$  and sunlight.

Without a catalytic converter, HC exhaust emissions decreased with increasing RME percentage. In contrast, CO emissions increased. The catalytic converter reduced the emissions of HC as well as the emissions of carbon monoxide, which coincides with speciation results obtained by other researchers (17,18). The efficiency of the catalytic converter depends on the blend (Fig. 9). Although HC were reduced by the use of RME,  $\text{NO}_x$  and aldehydes increased. Other researchers have reported reductions in aldehydes when using biodiesel (17,18). These contrary tendencies did not allow a theoretical comparison of the ozone-forming potentials of RME and DF (26). Therefore, the levels of ozone precursors in the exhaust emissions of both fuels were compared as discussed below.



**FIG. 9.** Emissions of carbon monoxide and hydrocarbons (HC) with and without catalytic converter for different blends; Farymann test engine, five-mode test. See Figure 2 for other abbreviation.



**FIG. 10.** Emissions of ozone precursors; Fendt tractor, five-mode test. See Figure 2 for abbreviation.

HC in varying concentrations of several magnitudes with a limit of detection in the parts per trillion range were detected by the GC-MS system used. A detailed description of the sampling procedure was given by Schröder *et al.* (21). The total emissions of individual HC are shown in Figure 10. Because of the large number of compounds in the emissions, aldehydes, aromatics, and alkenes including ethyne are shown as classes of compounds. The compounds are listed in Table 3 in the order (bottom to top) in which they appear in Figures 10 and 11. The data in Figure 10 indicate that compounds with low carbon numbers dominated emissions and that DF emissions contain less ethene and ethyne than do RME emissions. On the other hand, DF caused higher propene emissions. No explanation is currently available for these observations. Similar emissions of  $\text{C}_2$  HC but increased emissions of  $\text{C}_3$  were reported in other emissions tests (17,18).

In the five-mode test, RME raised the emissions of ozone precursors approximately 20%, with the catalytic converter reducing emissions as expected. To estimate the ozone-forming potential of the emissions, the concept of the specific maximal incremental reactivity (MIR) of individual compounds is useful. MIR values were given by Carter (27). A

**TABLE 3**  
Compounds Quantified in Figures 10 and 11 in Bottom-to-Top Order

Aldehydes and ketones	Aromatics	Alkenes
Hexanal		Isoprene
Benzaldehyde		1-Pentene
Isobutyraldehyde		<i>cis</i> -2-Pentene
Butanone	1,2,4-Trimethylbenzene	<i>trans</i> -2-Pentene
Propionaldehyde	1,3,5-Trimethylbenzene	<i>cis</i> -2-Butene
Acrolein	<i>o/p</i> -Xylene	<i>iso</i> -Butene
Acetone	<i>m</i> -Xylene	<i>trans</i> -2-Butene
Acetaldehyde	Ethylbenzene	1,3-Butadiene
Formaldehyde	Toluene	1-Butene
	Benzene	Propene
		Ethyne
		Ethene

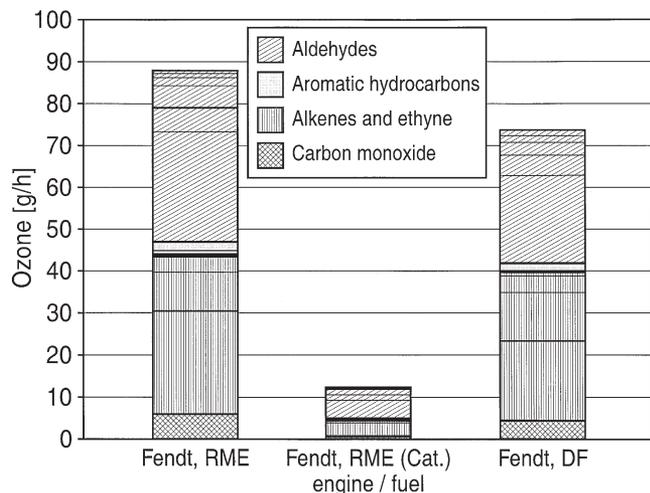


FIG. 11. Calculated ozone-forming potentials of diesel fuel and biodiesel exhaust emissions; Fendt tractor, 5-mode test. See Figure 2 for abbreviations.

comparison between emissions and their ozone-forming potential showed that alkenes and aldehydes have the most impact relevant to ozone formation, whereas aromatics have a lower percentage (Fig. 11). The MIR value of carbon monoxide (0.07 g ozone per g component) is more than 100 times smaller than the MIR value of ethene (9.97 g ozone per g component) or formaldehyde (9.12 g ozone per g component). However, because of the high mass of emitted CO, its ozone-forming potential was also taken into account.

In summary, no optimal blend for minimizing emissions was found. On the other hand, no blend with maximal negative effects on the composition of exhaust emissions exists. The advantages and disadvantages of RME changed in a linear fashion with the blend level. Only PM showed a nonlinear trend in one mode. The mutagenic potential of PM from RME was significantly reduced compared with conventional DF, although the gravimetric PM value from RME was higher. Benzene emissions increased with RME level. Biodiesel had a slight disadvantage in terms of  $\text{NO}_x$  and ozone precursors; however, significant soot reduction was observed that is responsible for the lower mutagenic potential of biodiesel PM. The dependence of the catalytic conversion ratio on blends indicated that the adaptation of fuels (blends) to the exhaust gas treatment may be a useful way to reduce emissions. Future research on particle-size distribution and particle number may reveal additional effects on human health and the environment that will help to use biodiesel more efficiently. The results also show that the fuel must be tailored to the engine and the catalyst. Systematic fuel research is therefore necessary.

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